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Investigation of the stability of Mn_{12} single molecule magnets

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Abstract The stability of single crystals and monolayers of Mn_{12} single molecule magnets under the influence of X-ray radiation and other possibly disruptive influences has been investigated by means of synchrotron radiation. Clear evidence for radiation induced sample degradation was found for both single crystals and monolayers. The comparison with spectra obtained after damaging the molecules by Ar^+ sputtering, metal evaporation or water moistening indicates a possibility to distinguish between radiation damage and other external influences. The results clarify some of the previous conflicting reports on the integrity of Mn_{12} molecules deposited on surfaces and are linked to the investigations aiming at studies of the electronic and magnetic properties of individual Mn_{12} clusters.

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1 Introduction

Single molecule magnets (SMMs) like Mn_{12} acetate [1–4] and its derivatives have attracted much attention as fundamental aspects of quantum effects in magnetism can be studied on these systems. In principle, Mn_{12} SMMs could be used as basic units for data storage or quantum computing [5]. The magnetic properties of bulk Mn_{12} SMMs have been extensively studied during the past decade [6, 7]. However, experiments on the magnetic properties of individual Mn_{12} molecules require the ability to deposit and address intact molecules on a surface. With respect to this, there have been several approaches to graft Mn_{12} molecules on different surfaces [8–14]. However, the conservation of the structural, electronic, and magnetic properties of Mn_{12} SMMs upon deposition on surfaces could not be unambiguously confirmed so far. X-ray absorption spectroscopy (XAS), resonant photoemission spectroscopy (RPES), and X-ray magnetic circular dichroism (XMCD) are useful techniques to probe the electronic structure of the Mn_{12} core and the magnetic properties of Mn_{12} molecules [15–18]. Nevertheless, there are conflicting reports on the structural integrity of Mn_{12} molecules deposited on surfaces. The authors of [17] claim that the deposition procedure does not affect the intimate cluster nature while the results of [18] indicate a degradation of a different Mn_{12} molecule after direct deposition on the Au(111) surface. A decoupling of the molecules from the substrate by means of a functionalization layer seems to allow the deposition of partially intact Mn_{12} molecules [18]. This ambiguity has to be resolved since any experiments on Mn_{12} molecules on surfaces require definite knowledge about the integrity of the Mn_{12} core.

To clarify this ambiguity, we performed a series of XAS measurements on single crystals and monolayers of different Mn_{12} derivatives at room temperature as well as under cryogenic conditions. Evidence for sample degradation as a function of exposure time was found for all Mn_{12} samples. The results indicate a possibility to distinguish between sample degradation due to radiation or to an inappropriate wet chemical sample preparation and clarify some of the previous conflicting reports on the integrity of Mn_{12} molecules on surfaces. The insights reveal the possibility that the integrity of Mn_{12} molecules can be conserved during certain deposition procedures.

2 Experimental details

Mn_{12}-biphenylcarboxylate ($Mn_{12}O_{12}(O_2CC_6H_4C_6H_5)_{16}(H_2O)_4$; Mn_{12}-biph), Mn_{12}-thiophenecarboxylate ($Mn_{12}O_{12}(O_2CC_4H_3S)_{16}(H_2O)_4$; Mn_{12}-th), and Mn_{12}-parafluorobenzoate ($Mn_{12}O_{12}(O_2CC_6H_4F)_{16}(EtOH)_4$; Mn_{12}-pfb) were synthesized as described elsewhere [19–21]. The single crystals were characterized by means of X-ray diffraction, MALDI-TOF mass spectrometry, IR spectroscopy, and SQUID. The samples revealed all signatures of a Mn_{12} SMM. Figure 1 shows an image of the Mn_{12} core, comprising eight Mn^{3+} and four Mn^{4+} ions.

As XAS probes the topmost layers of the sample, the single crystals were dissolved in dichloromethane (DCM) and recrystallized on a Au-covered Si plate with Ti adhesion layer (Au/Ti/Si) [22] to avoid any influences from surface decomposition during storage or transport of the material. A monolayer of Mn_{12}-pfb was grafted to Au/Ti/Si via a ligand exchange reaction with 4-mercapto-tetrafluorobenzoic-acid (4-MTBA) as described elsewhere [21]. XAS measurements were performed at the Russian–German beamline (RGBL) as well as at the PM-3 beamline at BESSY (Berlin) and at the D1011 beamline at MAX-lab (Lund). The RGBL/D1011 beamlines were operated in a low-flux mode

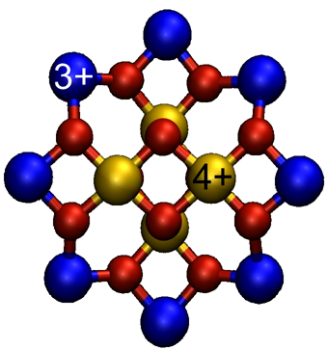

Fig. 1 (Color online) Representative image of the Mn_{12} core comprising eight Mn^{3+} (*blue*) and four Mn^{4+} (*yellow*) ions. Oxygen ions are depicted in *red*

providing radiation with a photon flux of about 10^{10} photons/s (energy range of 600–700 eV, spot size 1–2 mm^2). Measurements at these beamlines were performed at room temperature. The photon flux of the PM3 beamline was estimated to be at least 1 order of magnitude larger than at the D1011/RGBL beamline due to the different beamline optics and the smaller spot size (0.25 mm^2). Measurements at the PM3 beamline were performed at room temperature as well as under cryogenic conditions down to 10 K. XAS spectra were obtained in total electron yield mode with a resolution of about 100 meV full width at half maximum for D1011/RGBL and $E/\Delta E = 10000$ for PM3. The duration of a single XAS scan was 7–15 min. The base pressure was below 1×10^{-9} mbar for all the measurements. Further details of the experimental setup and data analysis are reported elsewhere [23].

The sample degradation due to X-ray radiation was investigated by illuminating the respective sample for a given time before recording XAS spectra. Sample degradation due to water moistening was investigated by exposing Mn_{12}-pfb monolayers on a Au/Ti/Si plate (cooled by DCM evaporation) to a humid atmosphere and recording an XAS spectrum. Degradation due to sputtering was investigated by sputtering Mn_{12}-pfb single crystals with Ar^+ ions at 1 keV for 5 min and recording an XAS spectrum. Degradation due to metal evaporation was investigated by evaporating Ti from a Ti sublimation pump filament oriented towards the sample for 90 s and subsequently recording an XAS spectrum.

3 Results and discussion

Figure 2 shows the time evolution of the XAS spectrum of a Mn_{12}-pfb single crystal, the final spectra obtained from Mn_{12}-th and Mn_{12}-biph single crystals, a spectrum obtained from a MnO sample that has not been sputtered prior to the measurement and a spectrum obtained from a monolayer of Mn_{12}-pfb on 4-MTBA/Au.

For $t = 0$, the spectrum of Mn_{12}-pfb single crystals is identical to previously reported spectra [15, 16, 18] thus being evidence for an intact Mn_{12} core comprising eight Mn^{3+} and four Mn^{4+} ions (see Fig. 1). After 15 min a more intense spectral contribution corresponding to Mn^{2+} is visible thus indicating a reduction of Mn ions to Mn^{2+}. The spectrum obtained after 200 min reveals a mixed $Mn^{2+/3+}$ signature. This spectrum was found to represent the final spectral line shape. The spectra were recorded at the D1011 low-flux beamline. On the other hand, the spectra of Mn_{12}-biph and Mn_{12}-th were recorded at the PM3 beamline. Sample degradation was observed within less than 2 min which can be attributed to the higher photon flux. No difference between measurements performed at $T = 300$ or 10 K (PM3) could

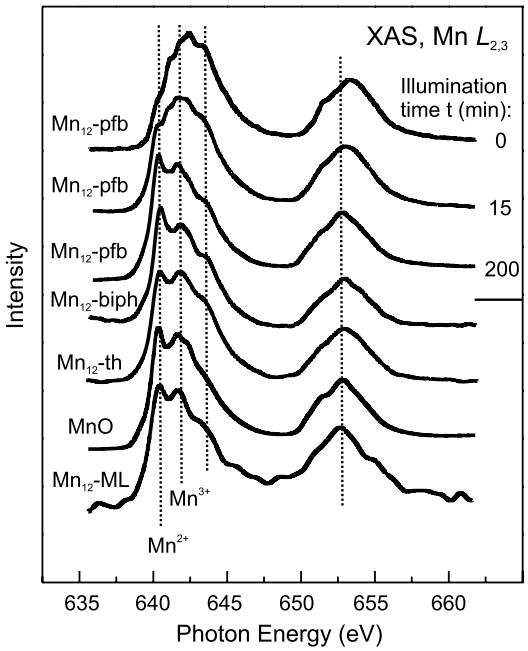

Fig. 2 XAS spectra of Mn_{12}-pfb, Mn_{12}-biph, Mn_{12}-th single crystals, and nonsputtered MnO showing the time evolution of the spectral line shape of Mn_{12}-pfb ($T = 300$ K, D1011) as well as the final line shapes of Mn_{12}-biph and Mn_{12}-th ($T = 10$ K, PM3), all revealing a mixture of $Mn^{2+/3+}$ signatures. The *bottom* spectrum (Mn_{12}-ML) was obtained from a monolayer of Mn_{12}-pfb on 4-MTBA/Au

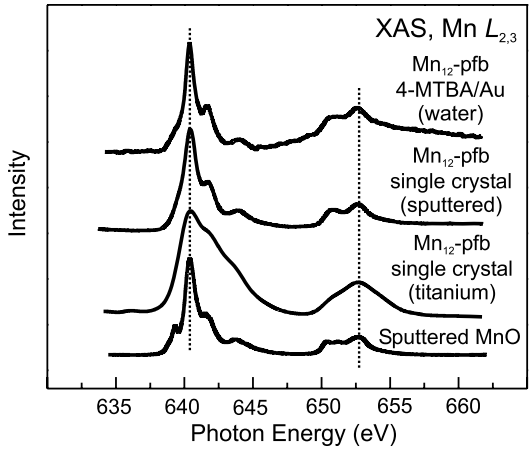

Fig. 3 XAS spectra ($T = 300$ K) of water-covered, Ar^+-sputtered (D1011) and titanium-covered (PM3) Mn_{12}-pfb revealing a dominant Mn^{2+} contribution. The spectrum of sputtered MnO (pure Mn^{2+}, RGBL) is shown for comparison

be observed. Time-resolved XAS measurements on Mn_{12}-th were also recorded at the RGBL beamline (not shown), revealing a degradation time of about 30 min. The XAS spectrum of MnO is shown for comparison since nonsputtered MnO is known to include Mn^{2+} and Mn^{3+} contributions due to a partial oxidation from Mn^{2+} to Mn^{3+} [24]. The comparison shows that the final spectral line shape of Mn_{12} single crystals is dominated by Mn^{2+} and Mn^{3+} rather than Mn^{3+} and Mn^{4+} which is an evidence for radiation-induced sample degradation. Nonetheless, the spectrum obtained from the Mn_{12}-pfb monolayer is identical to the spectra obtained from the Mn_{12} single crystals. This may indicate that a previously intact Mn_{12} monolayer was degraded due to radiation. A significantly shorter degradation time in the case of monolayers can be explained by the larger amount of secondary electrons emitted from Au(111) compared with the Mn_{12} single crystal environment. No proof for the identity of the source material is feasible. However, this interpretation may be supported by an intended destruction of Mn_{12} molecules and comparison of the XAS spectra as well as scanning tunneling microscopy (STM) measurements (see below).

Figure 3 shows a comparison of XAS spectra obtained from a monolayer of Mn_{12}-pfb on 4-MTBA/Au that has intentionally been covered with water, from Mn_{12}-pfb single crystals that have been Ar^+-sputtered or covered with titanium and from an Ar^+-sputtered MnO sample. The spectra obtained from water-covered or sputtered Mn_{12}-pfb samples reveal predominantly Mn^{2+} contributions as can be seen from the comparison with the MnO spectrum. This is a clear evidence for complete degradation of the Mn_{12} core. The spectrum obtained from the Ti-covered Mn_{12}-pfb sample is slightly different from the previous ones with small Mn^{3+} contributions being present. This can be assigned to an incomplete Ti coverage of the Mn_{12} single crystals or to a less drastic Mn_{12} core distortion. However, this spectrum is also different from those obtained from radiation-damaged Mn_{12} (see Fig. 2).

From the comparison of Figs. 2 and 3, it is obvious that any external influence—different from radiation—results in a predominant Mn^{2+} contribution. In particular, even the presence of small amounts of water during the monolayer deposition results in degradation of Mn_{12} molecules due to hydrolysis (see below). In contrast, the similarity between the final spectral line shapes of monolayers on functionalized surfaces (deposited in dry atmosphere) and single crystals (Fig. 2) may be interpreted as an indication that both spectral shapes are exclusively due to radiation damage and that the monolayer was deposited intactly. This is supported by the fact that the possibly radiation-induced final line shape (Fig. 2) is similar to a XAS spectrum presented in [17] where a monolayer of a Mn_{12} derivative with long alkyl chain ligands has been investigated. The comparison shows that the molecules [17] have also apparently been degraded by radiation. Nonetheless, this observation is consistent with the results from STM measurements [10, 18, 21]. Homogeneous layers of apparently intact molecules were reported in [10, 21]. In contrast, the direct deposition of Mn_{12}-th on Au(111) yielded STM images of diffuse clusters [18], thus indicating a fragmentation in agreement with previous XAS measurements at the RGBL beamline [18].

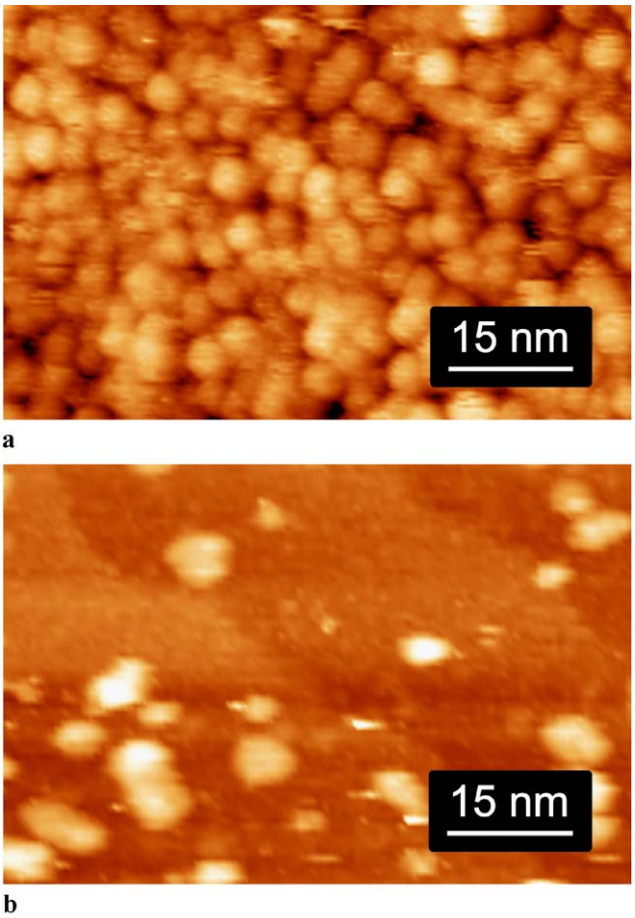

Fig. 4 (Color online) Comparison of STM images obtained from (**a**) Mn_{12}-pfb/4-MTBA deposited in a dry nitrogen atmosphere (XAS, see Fig. 2) and (**b**) Mn_{12}-pfb/4-MTBA deposited in a humid atmosphere (XAS, see Fig. 3)

Furthermore, the importance of excluding humidity during the preparation of Mn_{12} monolayers is corroborated. Figure 4 shows a comparison of two STM images obtained from (a) Mn_{12}-pfb/4-MTBA prepared under strict exclusion of water and (b) Mn_{12}-pfb/4-MTBA prepared in a humid atmosphere. Figure 4a shows a monolayer of intact Mn_{12} molecules. XAS spectra obtained from such samples revealed the mixed $Mn^{2+/3+}$ signature (Fig. 2), thus indicating degradation due to radiation. The shapeless clusters in Fig. 4b indicate a degradation of the molecules due to hydrolysis. XAS spectra obtained from such samples revealed the pure Mn^{2+} signature (Fig. 3), thus indicating degradation during the monolayer preparation. The consistency between XAS and STM measurements corroborates the need for advanced investigation techniques in the case of Mn_{12} on surfaces. In most previous investigations, the integrity of the Mn_{12} molecules was investigated on the basis of STM images that do not provide sufficient information about the integrity of Mn_{12} molecules as well as X-ray photoelectron spectroscopy that does not provide sufficient information about the valence state of Mn ions. These facts may indicate why there have been conflicting reports about the integrity of Mn_{12} single molecule magnets deposited on surfaces.

4 Conclusions

In conclusion, the stability of Mn_{12} single molecule magnets, both in the crystalline and monolayer environment, has been investigated by means of X-ray absorption spectroscopy at room temperature and under cryogenic conditions performed at three different synchrotron facilities. Clear evidence for X-ray radiation damage was found, resulting in a mixed signature of $Mn^{2+/3+}$. On the other hand, damaging by means of direct metal evaporation, Ar^+ sputtering or water coverage results in a predominant Mn^{2+} contribution that is significantly different from the radiation-induced one. The comparison with the actual STM images as well as previous XAS/STM results indicates that Mn_{12} molecules may retain their integrity during the deposition on two conditions: (1) Selection of an appropriate derivative as well as deposition protocol and (2) deposition under strict exclusion of disruptive influences like a humid atmosphere. The presence of Mn^{2+} in XAS spectra may be solely assigned to radiation damage. The results contribute to a clarification of some of the previous conflicting reports on the integrity of Mn_{12} single molecule magnets on surfaces.

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